

# Photoemission Quasiparticle Spectra of $\text{Sr}_2\text{RuO}_4$

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Multiband quasiparticle calculations based on perturbation theory and dynamical mean-field methods show that the creation of a photoemission hole state in  $\text{Sr}_2\text{RuO}_4$  is associated with a highly anisotropic self-energy. Since the narrow Ru-derived  $d_{xz,yz}$  bands are more strongly distorted by Coulomb correlations than the wide  $d_{xy}$  band, charge is partially transferred from  $d_{xz,yz}$  to  $d_{xy}$ , thereby shifting the  $d_{xy}$  Van Hove singularity close to the Fermi level.

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Angle-resolved photoemission spectroscopy is one of the key techniques providing detailed information on the Fermi surface topology of high temperature superconductors. In the layered copper oxide compounds (cuprates) high-resolution photoemission spectra can be obtained below and above the superconducting transition temperature and for different hole doping regimes. Although de Haas–van Alphen (dHvA) experiments in principle yield more reliable bulk Fermi surface data, they are less useful for the investigation of cuprates since they require extremely pure samples. Thus, it has so far not been possible for any of the high  $T_c$  cuprates to obtain consistent Fermi surface data from both photoemission and dHvA measurements.

The detection of superconductivity in  $\text{Sr}_2\text{RuO}_4$  [1] is of great importance since this system is the only layered perovskite compound known so far that is superconducting in the absence of copper and without requiring doping. Thus, a critical comparison of photoemission Fermi surface data with those derived from dHvA measurements is feasible. Surprisingly, independent studies of the dHvA effect [2] and angle-resolved photoemission [3–5] yield highly contradictory Fermi surface topologies. This discrepancy raises serious questions concerning the interpretation of photoemission data also in cuprate superconductors.

Because of the layered structure of  $\text{Sr}_2\text{RuO}_4$ , the electronic bands close to the Fermi level may be qualitatively understood in terms of a simple tight-binding picture. These bands are derived mainly from Ru  $t_{2g}$  states. The wide  $xy$  band exhibits two-dimensional character, while the narrow  $xz$  and  $yz$  bands are nearly one dimensional. All three bands are roughly  $2/3$  occupied, giving about 4 Ru  $d$  electrons per formula unit. Density functional calculations based on the local density approximation (LDA) [6,7] place the  $(\pi, 0), (0, \pi)$  saddle point Van Hove singularity of the  $xy$  band about 60 meV above the Fermi energy. Taking into account gradient corrections slightly lowers this singularity to about 50 meV above  $E_F$  [7]. Figure 1 provides a qualitative picture of the  $t_{2g}$  bands and of the Fermi surface exhibiting one hole sheet ( $\alpha$ ) and two electron sheets ( $\beta, \gamma$ ). Whereas the dHvA data [2] are consistent with these results, photoemission

spectra reveal a fundamentally different topology [3–5]: the  $xy$  Van Hove singularity near  $M$  appears below the Fermi level, converting the  $\gamma$  sheet from electronlike to holelike. Nevertheless, both experiments are reported to be in accord with Luttinger's theorem.

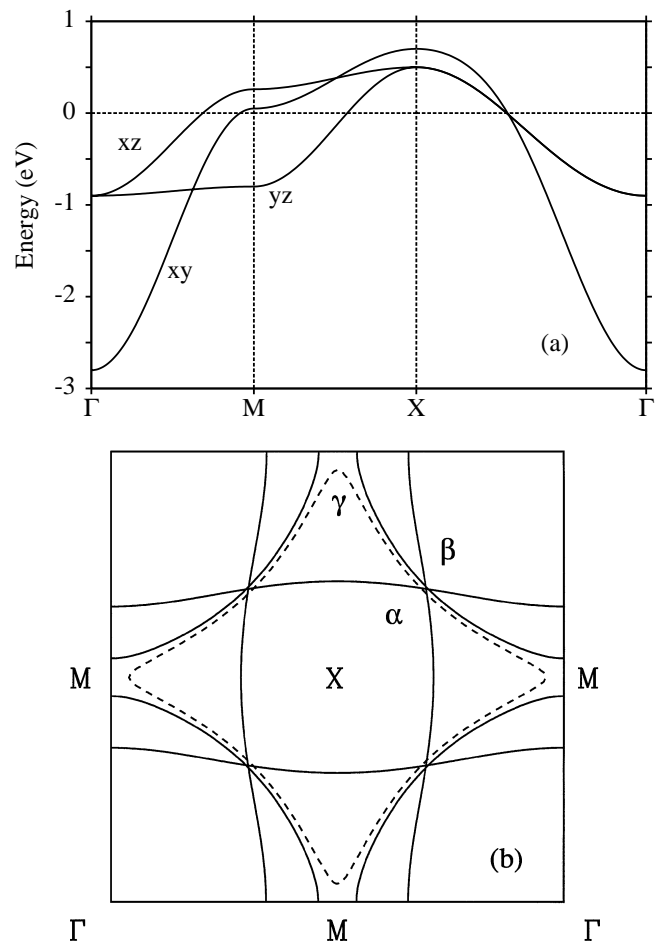


FIG. 1. (a) Dispersion of  $t_{2g}$  bands of  $\text{Sr}_2\text{RuO}_4$  in simplified two-dimensional Brillouin zone ( $E_F = 0$ ). (b) Solid lines: Fermi surface consistent with LDA band structure and dHvA measurements, with hole sheet  $\alpha$  and electron sheets  $\beta, \gamma$  (after accounting for hybridization). Dashed line: approximate  $xy$  Fermi surface derived from photoemission, indicating that  $\gamma$  is holelike.

Various effects have been proposed to explain this discrepancy between dHvA and photoemission data. (a) Since photoemission is surface sensitive, a surface-induced reconstruction associated with the breaking of bonds could lead to a modification of Ru-O hopping and a shift of  $t_{2g}$  bands. Estimates based on bulk calculations indicate that this mechanism could push the  $xy$  Van Hove singularity below  $E_F$  [7]. Actual surface electronic structure calculations for  $\text{Sr}_2\text{RuO}_4$  [8], however, show that this singularity remains above  $E_F$  even in the presence of surface relaxation. (b) Slightly different doping levels, temperatures, and magnetic fields used in both experiments could result in different Fermi surfaces, but these effects are believed to be too small to explain the main discrepancy [9]. (c) That the interpretation of the dHvA data is incorrect seems unlikely in view of the large body of experience available for this method. (d) The interpretation of the photoemission spectra, on the other hand, is nontrivial because of the quasiparticle character of the hole state created in the experiment. This aspect of the data has been ignored so far and is the focus of the present work.

According to the reduced dimensionality of  $\text{Sr}_2\text{RuO}_4$ , creation of a photohole should be associated with highly anisotropic screening processes which reflect the nature of the different electronic states involved. As shown in Fig. 1, the relevant bands near  $E_F$  comprise a roughly 3.5 eV wide band formed by in-plane hopping between Ru  $d_{xy}$  and O  $2p$  orbitals, and 1.4 eV narrow  $d_{xz}, d_{yz}$  bands. Assuming an on-site Ru  $dd$  Coulomb interaction  $U \approx 1.5$  eV, we have the intriguing situation:  $W_{xz,yz} < U < W_{xy}$ , where  $W_i$  is the width of the  $i$ th  $t_{2g}$  band. A value  $U \approx 1.5$  eV was in fact deduced from the observation of a valence band satellite in resonant photoemission from  $\text{Sr}_2\text{RuO}_4$  [10]. According to this picture, intra-atomic correlations have a much larger effect on the  $xz, yz$  bands than on the  $xy$  band, giving rise to a strongly anisotropic self-energy. Because of the  $\sim 2/3$  filling of the  $xz, yz$  bands, their narrowing, combined with Luttinger's theorem, leads to a charge flow from the  $xz, yz$  bands to the  $xy$  band. As we discuss below, for reasonable values of  $U$  this charge transfer is large

enough to push the  $xy$  Van Hove singularity close to or even below the Fermi level.

Since we are concerned with the qualitative influence of multiband correlations on quasiparticle spectra, we consider for simplicity two-dimensional next-nearest-neighbor tight-binding bands of the form  $\varepsilon(k) = -\varepsilon_0 - 2t_x \cos ak_x - 2t_y \cos ak_y + 4t' \cos ak_x \times \cos ak_y$ , where  $(\varepsilon_0, t_x, t_y, t') = (0.50, 0.44, 0.44, -0.14)$ ,  $(0.24, 0.31, 0.045, 0.01)$ ,  $(0.24, 0.045, 0.31, 0.01)$  eV for  $xy, xz, yz$ , respectively (see Fig. 1). These parameters ensure that the  $xy$  band has edges at  $-2.8$  and  $0.7$  eV, with a Van Hove singularity at  $0.05$  eV, and the  $xz, yz$  bands have edges at  $-0.9$  and  $0.5$  eV, with Van Hove singularities at  $-0.80$  and  $0.26$  eV, in agreement with the LDA band structure [7].

Next we specify the on-site Coulomb and exchange integrals which we use in the self-energy calculations discussed below. In the present case involving only  $t_{2g}$  states, there are three independent elements ( $i \neq j$ ) [11]:  $U = \langle ii | ii \rangle$ ,  $U' = \langle ij | ij \rangle$ , and  $J = \langle ij | ji \rangle = \langle ii | jj \rangle = (U - U')/2$ , where  $i = 1, \dots, 3$  refers to  $xy, xz, yz$ . Denoting by  $n_i$  the band occupations, the Hartree-Fock energies are  $\Sigma_1^{\text{HF}} = (n_1 + 4n_2)U - 10n_2J$  and  $\Sigma_{2,3}^{\text{HF}} = (2n_1 + 3n_2)U - 5(n_1 + n_2)J$ . As the band occupations  $n_i$  are rather similar, it is convenient to define the average occupation  $\bar{n}$ , so that  $n_1 = \bar{n} - 2\delta$ ,  $n_{2,3} = \bar{n} + \delta$ , and  $\Sigma_1^{\text{HF}} = 5\bar{n}(U - 2J) + 2\delta(U - 5J)$ ,  $\Sigma_{2,3}^{\text{HF}} = 5\bar{n}(U - 2J) - \delta(U - 5J)$ .

It is instructive to consider the second-order contribution to the local self-energy since the key point, namely, the large difference between the quasiparticle shifts of the  $xy$  and  $xz, yz$  bands, can already be illustrated in this approximation. Because the  $t_{2g}$  bands do not hybridize, the self-energy has no off-diagonal elements. The imaginary parts of the diagonal second-order Coulomb and exchange terms are given by

$$\text{Im}\Sigma_i(\omega) = \pi \sum_{jkl} R_{jkl}(\omega) \langle ij | kl \rangle [2\langle kl | ij \rangle - \langle kl | ji \rangle], \quad (1)$$

where

$$R_{jkl}(\omega) = \left( \int_0^\infty \int_{-\infty}^0 \int_{-\infty}^0 + \int_{-\infty}^0 \int_0^\infty \int_0^\infty \right) d\omega_1 d\omega_2 d\omega_3 \rho_j(\omega_1) \rho_k(\omega_2) \rho_l(\omega_3) \delta(\omega + \omega_1 - \omega_2 - \omega_3). \quad (2)$$

Here,  $\rho_j(\omega)$  denotes the single-particle density of  $t_{2g}$  states. Exploiting the symmetry properties of the Coulomb matrix elements, Eq. (1) reduces to

$$\text{Im}\Sigma_1(\omega) = U^2 R_{111}(\omega) + 2J^2 R_{122}(\omega) + 4(U'^2 + J^2 - U'J) R_{212}(\omega), \quad (3)$$

$$\text{Im}\Sigma_{2,3}(\omega) = (U^2 + 2U'^2 + 3J^2 - 2U'J) R_{222}(\omega) + J^2 R_{211}(\omega) + 2(U'^2 + J^2 - U'J) R_{112}(\omega). \quad (4)$$

The above expressions demonstrate that even for  $J = 0$  the self-energy of a given band depends on scattering pro-

cesses involving all three  $t_{2g}$  bands. Nevertheless,  $\Sigma_{xy}$  is dominated by interactions within the wide  $xy$  band or between  $xy$  and  $xz, yz$ . On the other hand,  $\Sigma_{xz,yz}$  primarily depends on interactions within the narrow  $xz, yz$  bands or between  $xz, yz$  and  $xy$ . These differences are a consequence of the layered structure of  $\text{Sr}_2\text{RuO}_4$  and give rise to anisotropic relaxation shifts.

For a more accurate description of charge transfer among quasiparticle bands, we include self-consistency in the spirit of dynamical mean-field theory [12]. In this scheme,  $\Sigma_i$  is a functional of the effective bath

Green's function  $G_i^{-1} = G_i^{-1} + \Sigma_i$ , where the local  $G_i$  is given by

$$G_i(\omega) = \int_{-\infty}^{\infty} d\omega' \frac{\rho_i(\omega')}{\omega + \mu - \Sigma_i(\omega) - \omega'}. \quad (5)$$

A typical frequency variation of  $\Sigma_i$  is shown in Fig. 2. Near  $E_F$ , the imaginary parts vary quadratically with frequency and the real parts satisfy  $\Sigma_{xz,yz} \gg \Sigma_{xy}$ ; i.e., the energy shift of the narrow  $xz, yz$  bands is much larger than for the wide  $xy$  band. Moreover, the difference  $\Sigma_{xz,yz} - \Sigma_{xy}$  at  $E_F$  is much larger than the difference between the Hartree-Fock energies  $\Sigma_{xz,yz}^{\text{HF}} - \Sigma_{xy}^{\text{HF}}$ .

Qualitatively similar results are derived from more refined treatments of on-site Coulomb correlations using multiband self-consistent quantum Monte Carlo (QMC) methods [12,13]. The temperature of the simulation was 15 meV with 128 imaginary time slices and  $\sim 300\,000$  Monte Carlo sweeps. Figure 3 shows the quasiparticle density of states  $N_i(\omega) = -\frac{1}{\pi} \text{Im} G_i(\omega)$ , obtained via maximum entropy reconstruction [14], together with the bare density of states  $\rho_i(\omega)$ . The Van Hove singularities near the edges of the  $xz, yz$  bands are shifted towards  $E_F$ , causing a sizable band narrowing. Because of the  $\sim 2/3$  filling of these bands, this effect is not symmetric, giving a stronger relaxation shift of the occupied bands than for the unoccupied bands. There is also some band narrowing of the  $xy$  bands, but since  $U < W_{xy}$  this effect is much smaller than for the  $xz, yz$  bands.

A crucial point is now that in order to satisfy the Luttinger theorem the more pronounced band narrowing of the  $xz, yz$  bands requires a transfer of spectral weight to the  $xy$  bands. Thus, the  $xy$  Van Hove singularity is pushed towards the Fermi level. In the example shown in Fig. 3, it lies about 10 meV above  $E_F$ , compared to 50 meV in the single-particle spectrum. We emphasize that this result is a genuine multiband effect where the filling of a relatively wide quasiparticle band is modified by correlations within other narrow bands of a different symmetry. Since the values of  $U$  and  $J$  are not well known, and considering the approximate nature of our single-particle bands and

self-energy calculations, it is not possible at the present to predict the exact position of the  $xy$  singularity. It is conceivable, therefore, that this saddle point might lie even closer to or below  $E_F$ .

As indicated in Fig. 1, the topology of the Fermi surface of  $\text{Sr}_2\text{RuO}_4$  depends critically on the position of the  $xy$  Van Hove singularity with respect to  $E_F$ . It is evident therefore that the charge transfer from  $xz, yz$  to  $xy$  due to the creation of the photohole must be taken into account when using angle-resolved photoemission to determine the shape of the Fermi surface. To compare our results with photoemission spectra, we show in Fig. 4(a) the dispersion of the  $t_{2g}$  quasiparticle bands along  $\Gamma M$  and  $MX$  derived from the spectral function  $A_i(\mathbf{k}, \omega) = -\frac{1}{\pi} \text{Im}[\omega + \mu - \varepsilon_i(\mathbf{k}) - \Sigma_i(\omega)]^{-1}$ . The  $xy$  Van Hove singularity at  $M$  lies 10 meV above  $E_F$ , so that considerable spectral weight appears below  $E_F$  in the immediate vicinity of  $M$ . To account for the finite energy resolution, and following the experimental procedure for determining the spectral weight near  $E_F$  [5], we show in Fig. 4(b) the Fermi surface obtained from the partially integrated spectral function  $\bar{A}_i(\mathbf{k}) = \int_{-\Delta}^{\Delta} d\omega A_i(\mathbf{k}, \omega + i\Delta)$  with  $\Delta = 25$  meV. Considering in addition the finite aperture of the detector (typically  $\pm 1^\circ$ , corresponding to  $\pm 5\%$  of  $k_{\parallel}$  near  $M$  for 25 eV photon energy), it is unavoidable to pick up spectral weight from occupied regions near  $M$ , even when the detector is nominally set at  $M$ . Thus, the near degeneracy of the  $xy$  singularity with  $E_F$  makes it extremely difficult using angle-resolved photoemission to determine the  $k$  point at which the  $xy$  band crosses the Fermi energy. Photoemission data taken with better energy and angle resolution might provide a more conclusive answer.

Figures 3 and 4 also show that due to the narrowing of the  $xz, yz$  bands, the weakly dispersive band is shifted from  $-0.8$  to about  $-0.4$  eV, in agreement with photoemission data [3–5]. For  $k_{\parallel}$  between  $M$  and  $X$ , this band is observed to cross  $E_F$  at about  $(\pi, 0.6\pi)$ , in good accord with our calculations. In addition, the calculations indicate the existence of a satellite below the  $xz, yz$  bands which might be

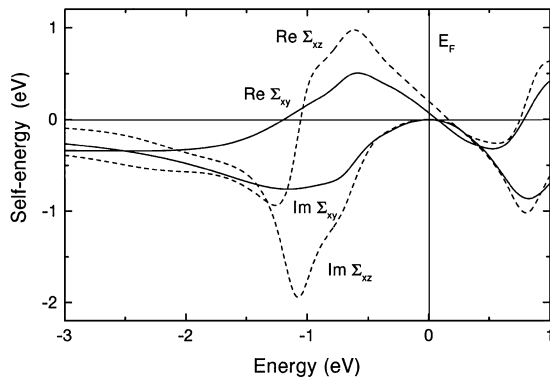


FIG. 2. Real and imaginary parts of self-consistent second-order self-energy for  $U = 1.2$  eV,  $J = 0.2$  eV. Solid curves:  $xy$ ; dashed curves:  $xz$ .

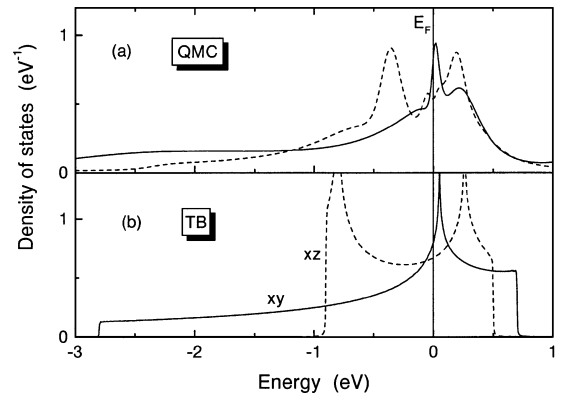


FIG. 3. (a) Quasiparticle density of states  $N_i(\omega)$  derived from self-consistent QMC scheme for  $U = 1.2$  eV,  $J = 0.2$  eV. (b) Single-particle density of states  $\rho_i(\omega)$  derived from tight-binding bands. Solid curves:  $xy$ ; dashed curves:  $xz$ .

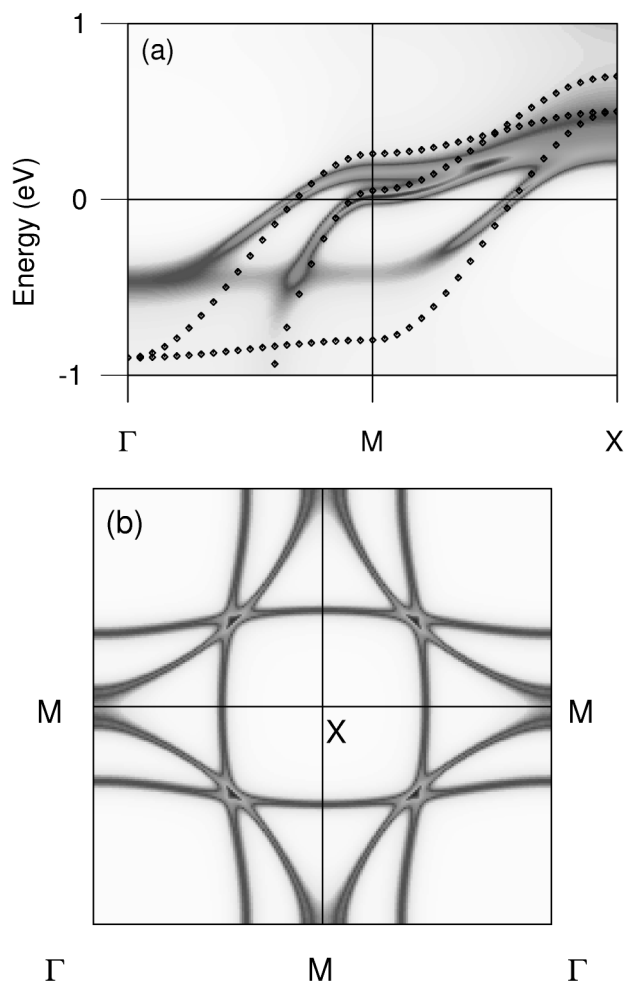


FIG. 4. (a) Quasiparticle bands along  $\Gamma M$  and  $MX$  derived from self-consistent second-order self-energy. Symbols: tight-binding bands. (b) Quasiparticle Fermi surface after accounting for energy broadening and resolution (see text).

related to the spectral feature observed near 2.5 eV binding energy using resonant photoemission [10]. The precise location of this satellite is difficult to determine because of the uncertainty of  $U$  and the approximate nature of our self-energy calculations.

Because of the proximity of the quasiparticle  $xy$  Van Hove critical point to the Fermi level, the imaginary part of the self-consistent self-energy exhibits a small linear contribution near  $E_F$ , indicating that the system may partially behave like a marginal Fermi liquid. In fact, in Eq. (3), it is only the first term  $\sim R_{111}(\omega)$  that gives rise to a linear term if the singularity coincides with  $E_F$ . As a result of multiband effects, however, this contribution is rapidly dominated by stronger quadratic terms involving the narrow  $xz, yz$  bands. Thus, we find the marginality to be rather weak.

We finally discuss the mass renormalization derived from our quasiparticle bands. For Coulomb and exchange matrix elements in the range  $U = 1.2\text{--}1.5$  eV,  $J = 0.2\text{--}0.4$  eV we find  $m^*/m \approx 2.1\text{--}2.6$ , in agreement with photoemission estimates  $m^*/m \approx 2.5$  [5], while dHvA

measurements [2] and specific heat data [15] suggest a factor of 3–4.

In summary, multiband quasiparticle calculations for  $\text{Sr}_2\text{RuO}_4$  show that the simultaneous existence of nearly one- and two-dimensional  $t_{2g}$  bands near  $E_F$  leads to a highly anisotropic self-energy of the photoemission hole state. Because of Luttinger's theorem, this anisotropy gives rise to a charge flow from the narrow  $xz, yz$  bands to the wide  $xy$  band, thereby shifting the  $xy$  Van Hove singularity very close to  $E_F$ . As a result, in the vicinity of  $M$  considerable spectral weight appears below  $E_F$ . These results might explain the controversial nature of recent photoemission data which have difficulty in determining whether or not the  $xy$  band at  $M$  is occupied.

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